

2023-01-01

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Turner, A

<http://hdl.handle.net/10026.1/20349>

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10.1016/j.envpol.2022.120492

Environmental Pollution

Elsevier BV

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## Lead and chromium in European road paints

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### ARTICLE INFO

#### Keywords:

Road paint  
XRF  
SEM-EDXS  
Pigments  
Microplastics  
Lead  
Chromium

### ABSTRACT

Lead chromate was commonly employed as a pigment in coloured road markings until restrictions led to the development of safer alternatives. In this study, the presence and concentrations of Pb and Cr have been determined in 236 road paints of various colours sampled from streets, highways, footways and carparks from eleven European countries. According to energy-dispersive X-ray fluorescence spectrometry, Pb was detected ( $>10 \text{ mg kg}^{-1}$ ) in 148 samples at concentrations up to 17.2% by weight, and above  $1000 \text{ mg kg}^{-1}$  yellow was the dominant paint colour. Lead concentrations on an area basis varied from 0.02 to  $8.46 \text{ mg cm}^{-2}$  and the metal was located at different depths amongst the samples, suggesting that formulations had been painted both recently and historically (and overpainted). Chromium was detected ( $>5$  to  $50 \text{ mg kg}^{-1}$ ) in 81 samples at concentrations between 20 and  $20,000 \text{ mg kg}^{-1}$  and most often in yellow paints, and concentrations co-varied with those of Pb. These observations, and results of scanning electron microscopy coupled with energy-dispersive X-ray spectrometry, suggested that heterogeneously dispersed  $\text{PbCrO}_4$  was the dominant, but not the only, Pb-based pigment in the samples. Although there were significant international differences in frequency of Pb detection and median Pb concentrations, overall, and despite various, albeit complex, regulations, recent or extant road paint pigmented with Pb and Cr remains a pervasive environmental problem and a potential health risk in many European countries.

### 1. Introduction

Metals that are known to be acutely and chronically toxic have been phased out or restricted in many manufactured products. In paints, lead (Pb) was employed extensively to enhance and stabilise colour, inhibit corrosion, reduce drying times and act as a fungicide (Gooch, 1993). However, the cumulative effects of the heavy metal on multiple organs, and in particular its impairment of the brain and nervous system in young children, have resulted in progressively wider and stricter regulations (O'Grady and Perron, 2011; Lucas et al., 2012; O'Connor et al., 2018). This has culminated in the Global Alliance to Eliminate Lead Paint initiative, a joint undertaking of the United Nations Environment Programme and the World Health Organization that promotes efforts to keep the Pb content in new paint as low as possible (and below  $90 \text{ mg kg}^{-1}$ ) (UNEP and WHO, 2012). Despite this initiative, and the voluntary phasing out of leaded products in paints by many industries and manufacturers, exemptions to regulations have been applied in certain industrial settings that include streets and highways (SAICM, 2014). Significantly, it was legal to use the pigment lead chromate,  $\text{PbCrO}_4$ , in

coloured road markings in the European Union (EU) until May 2019 when the EU Court overruled a European Commission derogation specific to this compound in certain applications (Speciation News, 2019). Lead chromate, or strictly, the family of yellow lead chromate pigments, also contains Cr(VI), a carcinogen that has no known minimum threshold level (Collins et al., 2010; Haney et al., 2014).

The composition, mineralogy, environmental dispersion and potential health impacts of road paints containing  $\text{PbCrO}_4$  have been reported for specific locations in Japan (Ozaki et al., 2004; Adachi and Tainosho, 2004), the US (White et al., 2014; O'Shea et al., 2021), South Korea (Lee et al., 2016, 2018) and Mexico (Meza-Figueroa et al., 2018) but there is a distinct lack of studies on road markings in Europe. Here, data appear to be limited to a few measurements of the Pb and Cr content of road paints in northwest England and southwest England as part of broader investigations of leaded paint in the urban setting (Sturges and Harrison, 1986; Turner and Solman, 2016; Turner and Lewis, 2018), and an assessment of road paint more generally as a source of microplastics, but not Pb, to the environment (Verschoor et al., 2016; Hann et al., 2018).

In the present study, we determine the concentrations of Pb and Cr in

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a wide range of road paints sampled throughout Europe, and both within and outside the EU. Over 200 paints of different colours, but mainly yellow, are measured by energy-dispersive X-ray fluorescence (XRF) spectrometry, with additional Pb measurements performed in an XRF mode that returns both the concentration on an area basis and an indication of the depth at which Pb is located in the sample. A range of Pb-positive paints is also analysed under a scanning electron microscope (SEM) with energy-dispersive X-ray spectrometry (EDXS) in order to gain an insight into surface morphologies and the microscopic location of metal-rich pigments. The findings provide a valuable assessment of the extent and scale of present, recent and historical applications of Pb and Cr in European road paints in order to assist with any inventories, risk assessments or decision-making.

## 2. Methods

### 2.1. Sampling

In the present study, road paint was defined as exterior paint used as a visible marking on publicly accessible roads and footways with a substrate of concrete, tarmac, paving, cobbles, stone, or, in the case of obstacles like drains and manholes, metal. Most markings were in a municipal setting (mainly urban and residential but some rural) with either the governing authority or a private contractor responsible for application and maintenance. Specific locations or facilities included streets, highways, bus lanes, bus stops, cycle paths, parks, schools, sports grounds, marinas and harbours, and carparks of supermarkets, visitor centres and hospitals.

In total, 236 samples of different colour (mainly white or hues of yellow, but also red, blue and green) were taken opportunistically from various locations and regions within eleven European countries (Table 1; Fig. 1). Most samples were collected by hand from locations where paint was in a deteriorating state and could be retrieved without dislodging or damaging the substrate. In some cases where paint was intact, thin scrapes were taken with the aid of a stainless steel chisel, taking care not to damage the integrity of the application. Samples were stored in individual polyethylene specimen bags and in the dark pending analysis.

### 2.2. SEM-EDXS analysis

Twenty samples of different origin and colour were analysed using a JEOL JSM-7001 F SEM equipped with JEOL EX-94300S4L1Q EDXS. Samples were mounted on aluminium stubs using double-sided conductive carbon tape and coated with C using low vacuum sputter coating. Imaging was performed with backscattered electrons whereby elements with high atomic number appear brighter in the image. EDXS measurements were performed with an accelerating voltage of 15 kV, a beam current of 1 nA and acquisition times up to 30 s, with an estimated detection limit of about 1% on a mass basis.

**Table 1**

Number and distribution of paint samples by country and colour. Also given are the districts or cities in each country where sampling took place.

Country	District/city	white	yellow	red	green	blue	total
United Kingdom	Merseyside, S Wales, SW England, N Yorkshire	14	48	5			67
Spain	Almeria, Girona and NE Spain, Madrid	12	30	4	4	3	53
Switzerland	Aargau, Geneva, Vaud	6	10	5	4	5	30
Luxembourg	Various towns	6	13	3	1	3	26
Belgium	Arlon, Brussels	4	8	3	2	4	21
France	Gaillard, Orsay, Thionville	2	5		1	1	9
Portugal	Faro, Lisbon	2	4		1		7
North Macedonia	Bitola, Ohrid, Skopje	1	5	1			7
Germany	Trier	4	2				6
Czech Republic	Prague	1	4				5
Greece	Thessaloniki		5				5
total		52	134	21	13	16	236

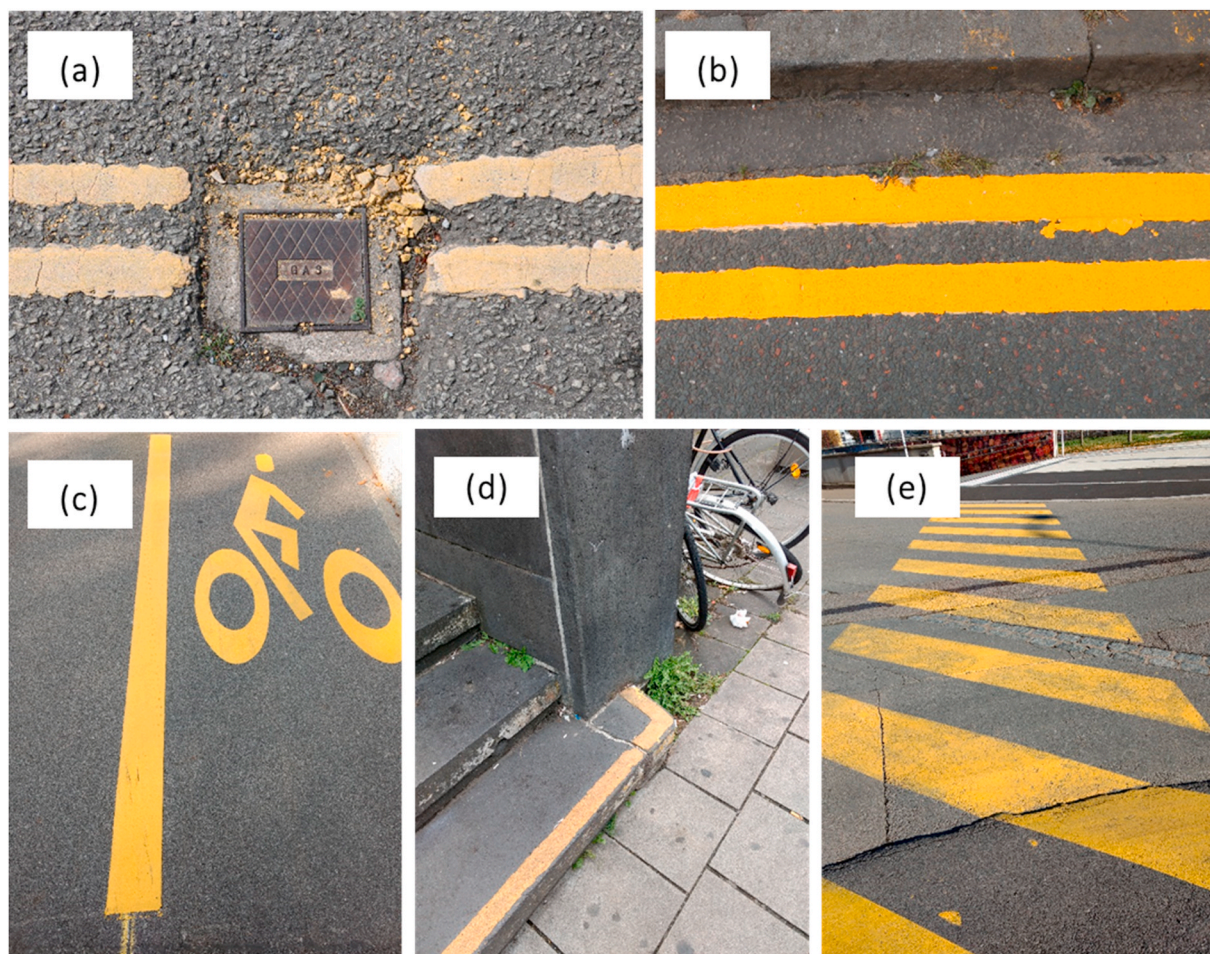
### 2.3. XRF analysis

Paint samples were analysed for a suite of elements ( $Z = 17$  to 83), of which Pb and Cr were the primary focus but Ba, Bi, Ca, Cd, Fe, Mo, Se and Ti are also considered, by standardless energy dispersive XRF spectrometry using a handheld Niton XL3t 950 He GOLDD + configured in a laboratory test stand. Samples were placed over the detector window on 3.6  $\mu\text{m}$  polyester film, with the outer surface (where evident) face down, and counted for 60 s. The majority of samples thicker than about 2 mm had a rigid structure and powdery texture (when crushed) and were counted in a mining-soil mode comprising successive counting periods of 30 s at 50 kV/40  $\mu\text{A}$  (main filter), 15 s at 20 kV/100  $\mu\text{A}$  (low filter) and 15 s at 50 kV/40  $\mu\text{A}$  (high filter). Most thinner samples were more elastic and pliable and were counted in a plastics mode with thickness correction for successive 30-s periods with the main and low filters. Presumably, differences between these two types of sample are related to the nature of the polymer resin, the means and thickness of application, and the presence and distribution of glass reflective beads and any packing additives or plasticisers (Burghardt et al., 2022). In both modes, fluorescent X-ray peaks for each element were converted to units of concentration on a mass basis ( $\text{mg kg}^{-1}$ ) and with an error of  $2\sigma$  using Niton fundamental parameters software.

To check for any concentration differences arising from the two XRF modes, about 200 samples of various thicknesses, colours and origins were counted by both approaches. For Pb, the results revealed a significant linear relationship ( $r^2 = 0.983$ ,  $p < 0.01$ ) and a slope of 0.737 that suggested the mining-soil mode returns concentrations that are, on average, about 25% lower than those returned by the plastics mode. For Cr, the relationship was more complex, with a near-unit slope at concentrations above 5000  $\text{mg kg}^{-1}$  but mining-soil mode returning progressively higher concentrations than the plastics mode as concentration decreased below this threshold. While these comparisons are informative, it must be borne in mind that discrepancies likely represent upper estimates of any errors introduced during our analyses. This is because thin, pliable samples were, by default, always analysed in the plastics mode, while thicker, powdery samples were always analysed in the mining-soil mode, with both modes independently verified by analysing reference materials of appropriate composition and texture (see below).

For 60 samples where Pb was detected, measurements were repeated for 20–30 s using a lead paint mode (high filter) that returns concentrations on an area basis ( $\text{mg cm}^{-2}$ ), the unit of measurement sometimes preferred or regulated from a health perspective (USEPA, 1995; Dixon et al., 2007). This mode also returns a depth index (from 1 to 10) that provides a semi-quantitative indication of the depth distribution of Pb (with increasing number signifying increasing depth).

For quality assurance purposes, various reference materials that were certified for concentrations of Pb and Cr on a mass basis and concentrations of Pb on an area basis were also analysed. Thus, the agricultural soil, NIST 2709, and stream sediment, GBW07318, returned concentrations in  $\text{mg kg}^{-1}$  within 15% of certified concentrations in the mining-soil mode; polyethylene discs, Niton PN 180–554 and PN



**Fig. 1.** Examples of yellow road paint sampled. (a) A powdery pale yellow formulation crumbling around a gas manhole cover in SW England, (b) a bright yellow-orange formulation that had recently been painted over a paler, older layer in S Wales, (c) demarcation of a cycle path in Geneva, Switzerland, (d) a painted step by a footway in Trier, Germany, and (e) a pedestrian crossing in Luxembourg. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

180–669, returned concentrations within 10% of certified concentrations in the plastics mode; and lead paint films, NIST 2579a, returned Pb concentrations in  $\text{mg cm}^{-2}$  that were within 5% of reference concentrations and depth indices of about 1.1 when analysed in the lead paint mode.

### 3. Results

#### 3.1. SEM imagery and EDXS results

Examples of SEM images of road paints that were Pb-positive according to XRF analysis (see below) are shown in Fig. 2. In most cases, the paints examined were highly heterogeneous and consisted of an organic matrix, sometimes containing glass reflective beads of 100 to 500  $\mu\text{m}$ , and finer (<40  $\mu\text{m}$ ) mineral particles or aggregates. When mineral particles were targeted, EDXS indicated a combination of one or more of the following elements: Al, Ba, Ca, Cl, Cr, Fe, Mg, Na, Pb, S and Ti; although it should be borne in mind that some of these elements may have also been picked up from surrounding material within the X-ray beam area. Lead and Cr, specifically, were simultaneously detected in small (<5  $\mu\text{m}$ ) pigmented particles that appeared bright white in the SEM images in back-scattering mode.

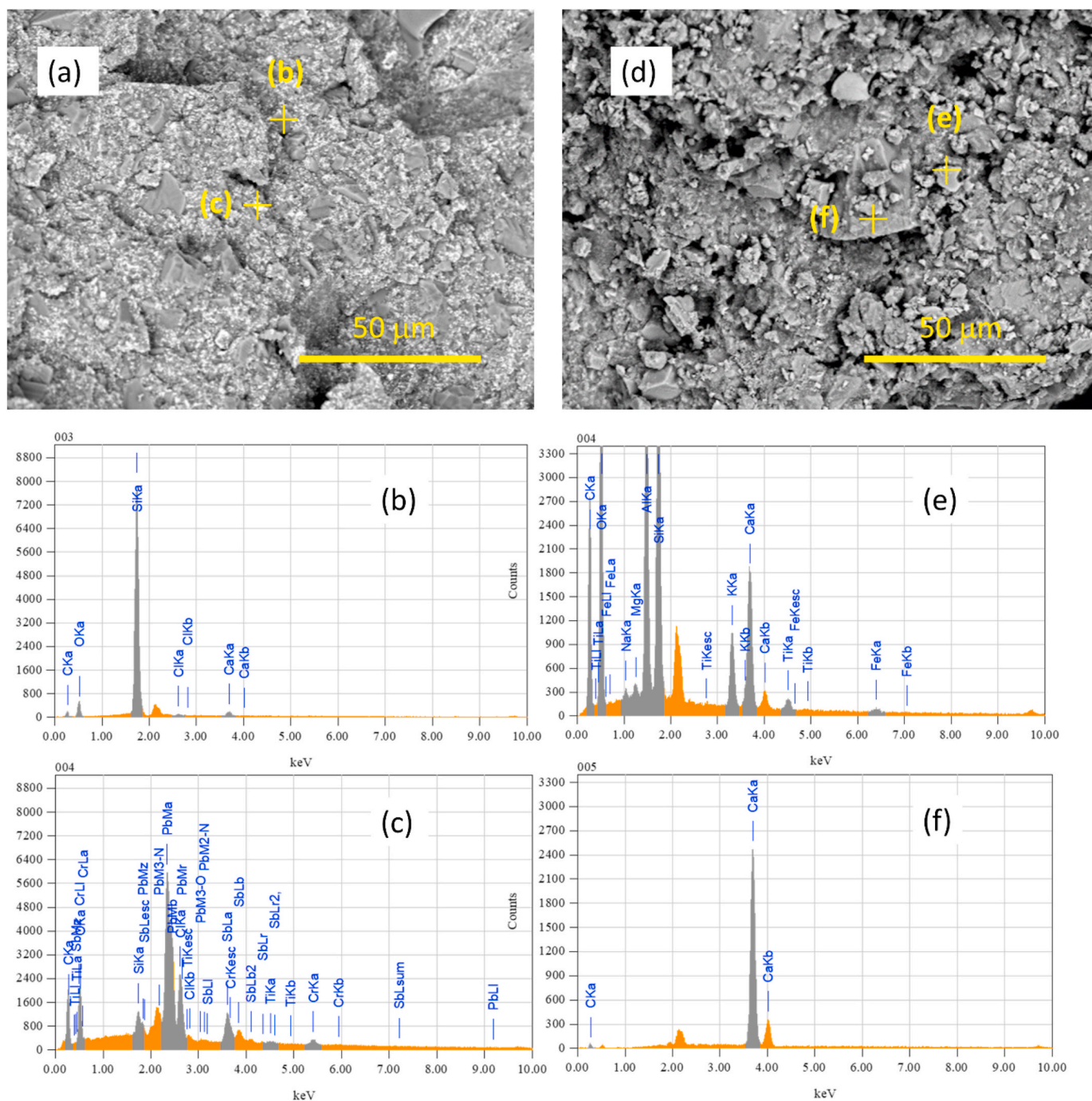
#### 3.2. Broad elemental composition by XRF analysis

An inspection of the (more quantitative, sensitive and

comprehensive) XRF data of “heavy” elements ( $Z > 17$ ) derived from the analysis of European road paints in the mining-soil mode (encompassing a wider range of elements and samples than the plastics mode) revealed that those most commonly present and at the highest (albeit variable) concentrations were Ba, Ca, Fe and Ti. Barium was detected (with a limit of detection, LOD, of  $\sim 100\text{--}500 \text{ mg kg}^{-1}$ ) in more than one-half of the paint samples embracing all colour categories, with EDXS results suggesting the presence of  $\text{BaSO}_4$ , and there were significant geographical differences. For example, the median concentrations for the Spanish and UK samples were  $45,400 \text{ mg kg}^{-1}$  and  $1370 \text{ mg kg}^{-1}$ , respectively ( $p < 0.01$  according to a Mann-Whitney  $U$  test). Calcium was detected in all samples at concentrations above several thousand  $\text{mg kg}^{-1}$ , with an overall median of  $200,000 \text{ mg kg}^{-1}$  and concentrations exceeding  $400,000 \text{ mg kg}^{-1}$  in six rather powdery paints that were different shades of yellow (maximum =  $460,000 \text{ mg kg}^{-1}$ ). Iron was detected in all samples with a median concentration of  $1660 \text{ mg kg}^{-1}$  and concentrations exceeding  $10,000 \text{ mg kg}^{-1}$  in 18 paints that encompassed all colours (but were usually yellow). Titanium was detected (LOD  $\sim 10 \text{ mg kg}^{-1}$ ) in all but five samples, with a median concentration of about  $6300 \text{ mg kg}^{-1}$  and concentrations exceeding  $100,000 \text{ mg kg}^{-1}$  in seven paints that were all white.

#### 3.3. Pb and Cr concentrations on a mass basis

With an LOD of about  $10 \text{ mg kg}^{-1}$ , Pb was detected in 148 road paint samples across all countries and colour categories and that had been



**Fig. 2.** (a) Back-scattered SEM image of a yellow road paint with EDXS spectra shown for sites (b) and (c), and (d) back-scattered SEM image of a white road paint with EDXS spectra shown for sites (e) and (f). Although there is often spectral interference from surrounding material, the dark grains in (b) and (f) appear to be calcite, the bright pigment in (c) appears to be  $\text{PbCrO}_4$  ([Pb] to [Cr] by mass  $\sim 5.3$ ), and the dark grain in (e) appears to be a more complex mineral particle. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

analysed in either the mining-soil mode or plastics mode (depending on sample thickness and characteristics). Detectable concentrations are shown in ascending order in Fig. 3, along with the colour of each sample and summary statistics. With increasing concentration (and up to 17.2% by weight) there is a clear decrease in colour distribution with yellow paints becoming dominant above  $1000 \text{ mg kg}^{-1}$ . With an LOD that was more variable (about  $5\text{--}50 \text{ mg kg}^{-1}$ ), Cr was detected in 81 samples from all countries, and with a concentration range from about 20 to  $20,000 \text{ mg kg}^{-1}$  (Fig. 3). The majority of Cr-positive paints were yellow ( $n = 67$ ) and there were no blue samples.

Concentrations of Pb are plotted against concentrations of Cr (where

both metals were detected;  $n = 78$ ) in Fig. 5. With the exception of two green, three white and six red samples, all paints were yellow, and overall there was a significant and slightly non-linear relationship between the two metals. In addition, there were three paint samples in which Cr was detectable (at below  $50 \text{ mg kg}^{-1}$ ) but Pb was not, and 70 samples in which Pb was detectable and Cr was not; the latter included six cases (yellow, white and green) where Pb concentrations exceeded  $1000 \text{ mg kg}^{-1}$ .

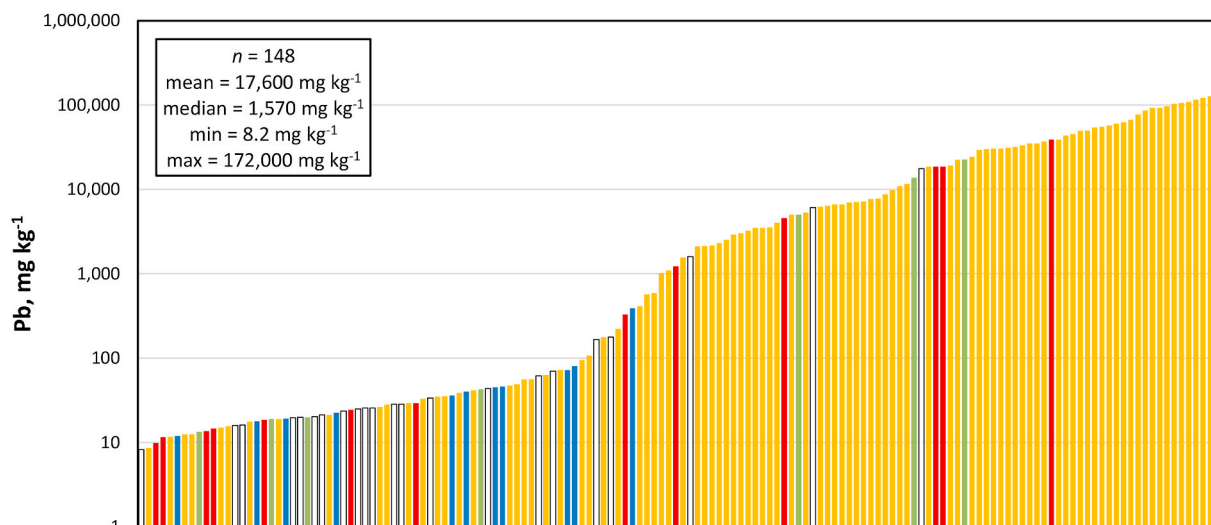


Fig. 3. Lead in European road paints, shown in order of ascending concentration and coded according to colour. Inset are summary statistics for the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

### 3.4. Pb concentrations on an area basis

For the samples analysed in the lead paint mode, statistical summaries of concentrations on a mass and area basis and the depth distribution of the metal within the paints are given in Table 2. The depth index provides a semi-quantitative measure of the depth of Pb in the sample, with increasing depth associated with an increasing index. Values close to 1 indicate Pb at the surface of a thin coating, such as the certified reference paint films (SRM 2579a) analysed for quality assurance purposes, while values approaching 10 signify that Pb is buried at a depth that is some function of the limit of penetration of primary X-rays and/or the return of secondary Pb lines. Values for the present samples range from 1.43 to 10 (with a median of about 2.2), reflecting variable depth distributions of leaded paint.

Samples returning the lowest and highest concentrations of Pb on an area basis (0.02 and 8.46 mg cm<sup>-2</sup>, respectively) were coincident with the corresponding samples with the lowest and highest concentrations on a mass basis (569 and 172,000 mg kg<sup>-1</sup>, respectively). However, the overall relationship between the two measures of Pb concentration was more complex (Fig. 6a), largely because the mining-soil and plastics modes return concentrations that may result from dilution of a single leaded layer by overlying (non-leaded) paint. Accordingly, when areal concentrations of Pb are normalised to depth index, the relationship with concentrations on a mass basis is greatly improved (Fig. 6b).

Different spatial and depth distributions of Pb (and Cr) also result in differences returned by XRF and EDXS. For instance, the yellow road paint in Fig. 2a returned Pb and Cr concentrations of about 120,000 and 11,000 mg kg<sup>-1</sup>, respectively, and a depth index for Pb of about 2. With Pb and Cr near to the surface in individual pigment particles, the metals are detectable by targeting these (bright) particles during EDXS analysis. By contrast, the white paint in Fig. 2d returned a Pb concentration of about 6000 mg kg<sup>-1</sup> and no detectable Cr, and a depth index for Pb of close to 10. Buried below a newer layer(s) of paint, therefore, the weaker

Table 2

A summary of Pb concentrations in mg kg<sup>-1</sup> and mg cm<sup>-2</sup> and Pb depth distributions (no units) for the 60 samples analysed in the lead paint mode.

	Pb, mg kg <sup>-1</sup>	Pb, mg cm <sup>-2</sup>	depth index
mean	40,200	2.59	2.96
median	30,000	2.34	2.19
min	569	0.02	1.43
max	172,000	8.46	10.0

and less penetrating X-rays of EDXS are unable to detect Pb.

## 4. Discussion

This study has shown that Pb and Cr are widely distributed in road paints of different colours (but mainly yellow) serving as various types of markings throughout Europe. Both metals can occur as general, extraneous contaminants of the urban or roadway environment, as contaminants introduced during paint manufacture, or as deliberately added compounds that serve some function in the dried matrix. Lead (and presumably Cr) is also widely distributed as a function of depth, and as an additive can occur within a single layer in a thin sample, or within a single or multiple layers in thicker samples where overpainting may have been practiced.

Our analyses do not allow us to empirically discriminate environmental or manufactured contaminants from additives in the samples but a threshold concentration of Pb can be used as an approximate indicator. While quantitative information on the Pb content of European road paints is lacking, in the US LeGalley et al. (2013) report Pb concentrations in extant paints of between about 800 and 6300 mg kg<sup>-1</sup> and White et al. (2014) and Gottesfeld (2015) suggest that concentrations between 20,000 and 50,000 mg kg<sup>-1</sup> may have been present in the original (dried) formulations. By contrast, in a remote, arid city in Mexico, the concentrations of Pb in extant paints was found to range from about 6000 to 80,000 mg kg<sup>-1</sup> (Meza-Figueroa et al., 2018) and a concentration of 12,000 mg kg<sup>-1</sup> has been reported for yellow road paint in a Japanese City (Ozaki et al., 2004).

Regarding our samples, there is a clear shift in the frequency distribution of Pb concentrations between 100 and 1000 mg kg<sup>-1</sup> (Fig. 3) which also coincides with an increase in the detection frequency of Cr. Thus, we define a measured concentration of >1000 mg kg<sup>-1</sup> of Pb (and equivalent to about 0.2 mg Pb cm<sup>-2</sup>) to signify the presence of the metal as a functional additive at or below the paint surface. On this basis, 78 paints tested (or about a third of the total) and embracing all colour types contain Pb as an additive, and of these, 36 contain Cr at a concentration greater than 1000 mg kg<sup>-1</sup>.

Consistent with the dominance of Pb and Cr in yellow samples (Figs. 3 and 4), the most important Pb-based pigments in road paints have been those in the chrome yellow family in which Cr exists as Cr(VI): namely, pure lead chromate, PbCrO<sub>4</sub>, the mixed phase pigment of lead chromate and lead sulphate (lead sulphochromate; Pb(Cr,S)O<sub>4</sub>), and the mixed phase pigment of lead chromate, lead sulphate and lead molybdate (lead chromate molybdate sulphate; Pb(Cr,S,Mo)O<sub>4</sub>). The mass

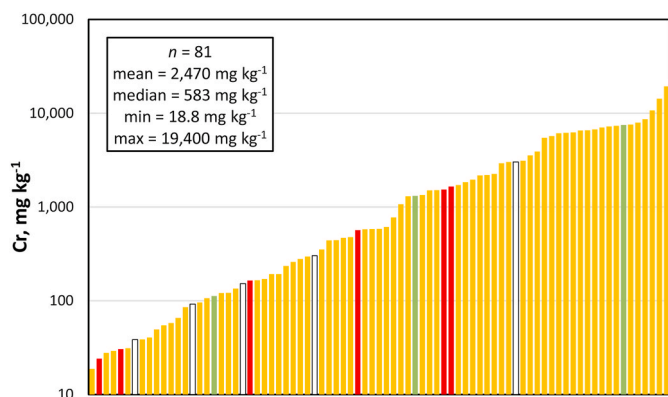


Fig. 4. Chromium in road paints, shown in order of ascending concentration and coded according to colour. Inset are summary statistics for the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

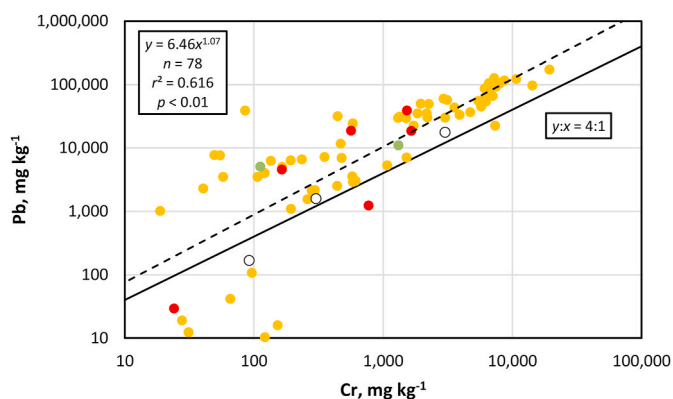


Fig. 5. Concentrations of Pb versus concentrations of Cr for European road paints coded according to colour. The solid line represents a ratio of 4:1, equivalent to the mass ratio of Pb:Cr in pure lead chromate, and the dashed line is the equation of best fit through the data. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ratio of Pb to Cr(VI) in pure lead chromate is about 4 and those for lead sulphochromate and lead chromate molybdate sulphate are higher by amounts dependent on the proportions of  $\text{PbCrO}_4$ ,  $\text{PbSO}_4$  and  $\text{PbMoO}_4$  present. Regarding the distributions of Pb versus Cr in Fig. 5 denoting yellow paints, there are two groups of data above a Cr concentration of  $1000 \text{ mg kg}^{-1}$ : firstly, some points are close to the line of 4:1, suggesting the presence of pure  $\text{PbCrO}_4$  as a pigment, and secondly, there are more scattered data lying above this line, suggesting the presence of mixed phase pigments. Since Mo was either not detected or only present at levels below  $50 \text{ mg kg}^{-1}$  we surmise that the latter data represent lead sulphochromate with a variable Pb:Cr ratio (but averaging about 9) that reflect different proportions of  $\text{PbCrO}_4$  and  $\text{PbSO}_4$  in the mixed pigment and, therefore, different shades of yellow, with the blue, iron-based pigment, Prussian blue, added in some cases to attain a green colour. For red samples, Pb:Cr ratios may not conform with either the pure or a mixed phase chrome yellow because of the additional presence of lead oxide (in the pigment, chrome red:  $\text{PbCrO}_4 \cdot \text{PbO}$ ) (Oldring, 2003). Regarding white paints that returned a Pb concentration above  $1000 \text{ mg kg}^{-1}$  ( $n = 3$ ; see Fig. 2d), measurements in the lead paint mode revealed that the metal was buried deeply in the samples (with depth indices at or just less than 10). We attribute this to the historical use of white lead ( $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ ) or basic lead sulphate ( $\text{PbSO}_4 \cdot \text{PbO}$ ) where Cr was not detected, or the presence of yellow chromate that had been overpainted by more recent white formulations.

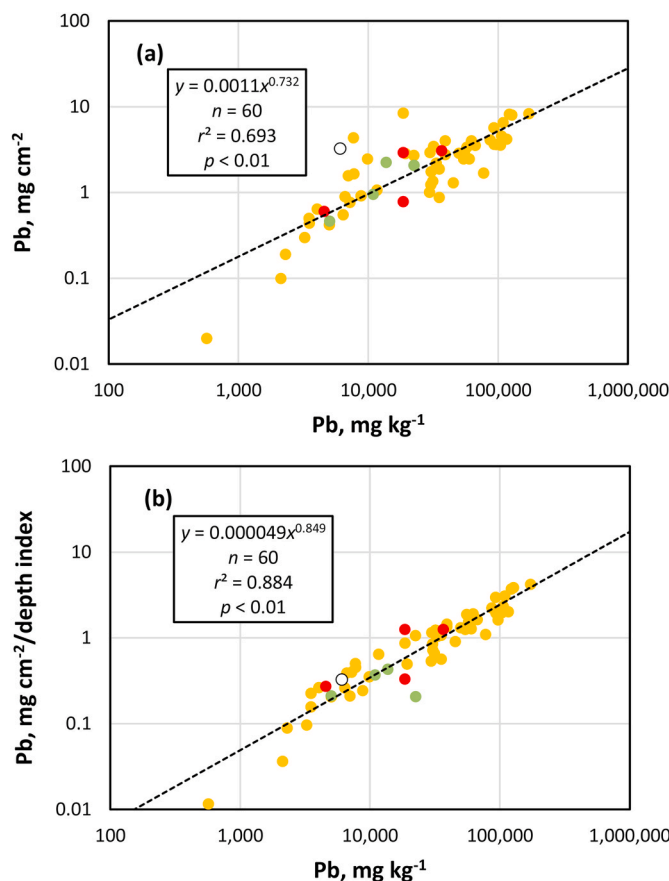


Fig. 6. Scatter plots of concentrations of Pb on a mass basis and concentrations of Pb (a) on an area basis and (b) on an area basis normalised to depth index. Dashed lines are best power fits whose equations are annotated.

Along with other compounds based on Pb, a neurotoxin, and/or chromate, a carcinogen, the pigments referred to above have been subjected to increasing restriction on health and environmental grounds, with paint manufacturers developing safer alternatives (ECHA, 2009; Kemsley, 2010). With respect to road paints, however, there are often exemptions or rather ambiguous regulations and guidelines. Thus, in some countries (e.g., South Korea), lead chromates were prohibited in road paints more than a decade ago (Lee et al., 2016) whereas in others (e.g., Chile and South Africa) lead chromates are still permitted for specific uses that include road painting (SAICM, 2014). In the US, road paint specification is dictated at a state level and while extensive nationwide testing suggests that lead chromates were phased out over a decade ago (White et al., 2014; Gottesfeld, 2015), the ready acquisition of lead-rich yellow road paints for recent experimental studies indicates that this may not necessarily be the case across the entire country (O'Shea et al., 2021).

In a few European countries, including Norway, lead chromates have been prohibited in yellow road paints for more than 20 years (InfoCuria, 2019) but within the EU their use was supposed to cease in May 2015 according to the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations (SAICM, 2014). However, the European Commission and REACH committee authorised the use of lead chromates for various industrial uses, including road paints, in 2016. The application was submitted by a pigment manufacturer based outside of the EU (Dominion Colour Corporation of Canada) and in road paints, lead chromates were authorised for four years. The legality of this authorisation was subsequently challenged by various parties, including the Swedish government, and in 2019 the EU Court ruled that Dominion Colour Corporation could no longer sell lead chromate pigments on the

EU market (Speciation News, 2019). The European Commission subsequently appealed the decision on the grounds of lack of suitable alternatives, but the European Court of Justice upheld the original court's findings (Chemical Watch, 2021). Thus, in individual EU member states it is difficult to determine when lead chromates were prohibited but, in theory, they could have been applied legally until 2019. With regard to North Macedonia (outside of the EU and its affiliates) and according to a report conducted by the Global Alliance for the Elimination of Lead Paint of the United Nations Environment Programme and the World Health Organization, there are restrictions on use of lead carbonate and lead sulphate but no mention is made of lead chromates (SAICM, 2014).

Despite these restrictions, and guidelines or recommendations at a national level (e.g., Royal Commission on Environmental Pollution, 1983), leaded road paint remains a pervasive problem in many European countries. In some cases, this paint may represent extant or over-painted deposits from old applications. However, the occurrence of Pb near to the surface of many samples and in what appeared to be relatively new coatings in private or modern settings (including, notably, supermarket carparks) and, more generally, timescales for repainting of three to five years (Kemsley, 2010), suggests that leaded paints may have also been used recently, despite safer alternatives being available. Alternative yellow pigments are mainly organic-based compounds that are proprietary (Kemsley, 2010) but our XRF analyses suggest that bismuth vanadate ( $\text{BiVO}_4$ ) is also being used in some countries (Pfaff, 2022). Alternative red pigments may also be organic, although we noted in one case (an urban street in Geneva) the application of an inorganic pigment based on another toxic metal and that has been subjected to increasing restrictions (cadmium sulphoselenide).

Through the physical wear, abrasion and deterioration of road paints, Pb- and Cr-rich fragments and dusts are readily formed (see Fig. 1, for example) which directly contaminate street dusts, storm water drainage, local water courses and biota like lichens (Adachi and Tainosho, 2004; Murakami et al., 2007; LeGalley et al., 2013; Meza-Figueroa et al., 2018; Dietrich et al., 2022). Fine particles of lead chromate and lead sulphochromate also have the potential for long-range (trans-boundary) transport (Lee et al., 2016) and, via inhalation, have the potential to reach the alveolar region of the lungs (Meza-Figueroa et al., 2018; O'Shea et al., 2021).

Despite the negligible solubility of lead chromate ( $K_{sp} = 2 \times 10^{-14}$ ), Pb in particular was found to be subject to significant dissolution from yellow road paint particles into solutions of salts, including NaCl and  $\text{CaCl}_2$ , that mimic road treatment conditions (White et al., 2014), meaning that this metal may be partially mobilised into aquatic receptors. Experiments performed with commercial chrome yellow suggest that dissolution may also be accelerated in the presence of sunlight and natural organic matter (Gao et al., 2019). By contrast, however, O'Shea et al. (2021) found little or no dissolution of Pb or Cr from road paints containing lead chromate into fluids that simulated rainwater and the human lung and digestive systems. The discrepancies were attributed to an amorphous silica coating on lead chromate particles in the latter study, meaning that silica encapsulation might, ultimately, be more critical to the environmental impacts of road paints than the content of Pb or Cr or the condition of the painted surface.

The bioaccessibility or environmental availability of Pb and Cr amongst the diversity of European road paints has not been tested but two factors are likely to be significant. Firstly, and as above, the presence or degree of any silica encapsulation, and secondly, and specifically for Pb, the presence of additional leaded compounds that are more soluble than lead chromate. Thus, in the studies above,  $\text{PbCrO}_4$  stoichiometry is measured or assumed, but our results suggest that lead sulphate, lead oxide and, in some white formulations, white lead might also be present. Clearly, further studies on a range of sample types would be required to address these factors.

## 5. Conclusions

This is the first study to systematically analyse the elemental content of road paints from Europe and, specifically, to document concentrations of Pb and Cr. The results of XRF and SEM-EDXS analyses indicate that heterogeneously dispersed lead chromate(s), at up to concentrations of about 20% by weight, has been widely used as a pigment in yellow paints on roads, highways, carparks and other public facilities. An assessment of the depth within the samples at which Pb was located suggests that the pigment has been applied both historically and recently. Regulations on the use of lead chromate within the EU have been ambiguous and contested over the past few years, while outside the EU guidelines and regulations (if any) vary between nations. Despite these restrictions, road paints pigmented with Pb and Cr remain a pervasive environmental problem and a potential health risk in many European countries.

## Credit author statement

AT: conceptualization; methodology; investigation; formal analysis; writing – original draft; writing – review and editing, MF: methodology; investigation; formal analysis; writing – original draft; writing – review and editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Acknowledgements

We are grateful to various friends and colleagues who assisted with sample collection. We thank James Quinn, University of Plymouth, and Agathe Martignier, University of Geneva, for technical assistance with the XRF and SEM-EDXS analyses, respectively.

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